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(54) Mouldable compositions

(57) A mouldable composition comprising a blend of a resilient thermoplastics material and *either* (i) a potentially-ionisable copolymer of ethylene and an α , β -unsaturated carboxylic acid which is ionised subsequent to the formation of the blend;

or (ii) an ionic copolymer of ethylene and an α , β -unsaturated carboxylic acid which is further ionised subsequent to the formation of the blend;

or (iii) an ionic copolymer of ethylene and an α , β -unsaturated carboxylic acid which is substantially ionised and which is powdered prior to the formation of the blend, in which the powdered copolymer (iii) has a maximum particle size of 200 microns and the total neutralisation level in said copolymer (i), (ii) or (iii) is at least 60%.

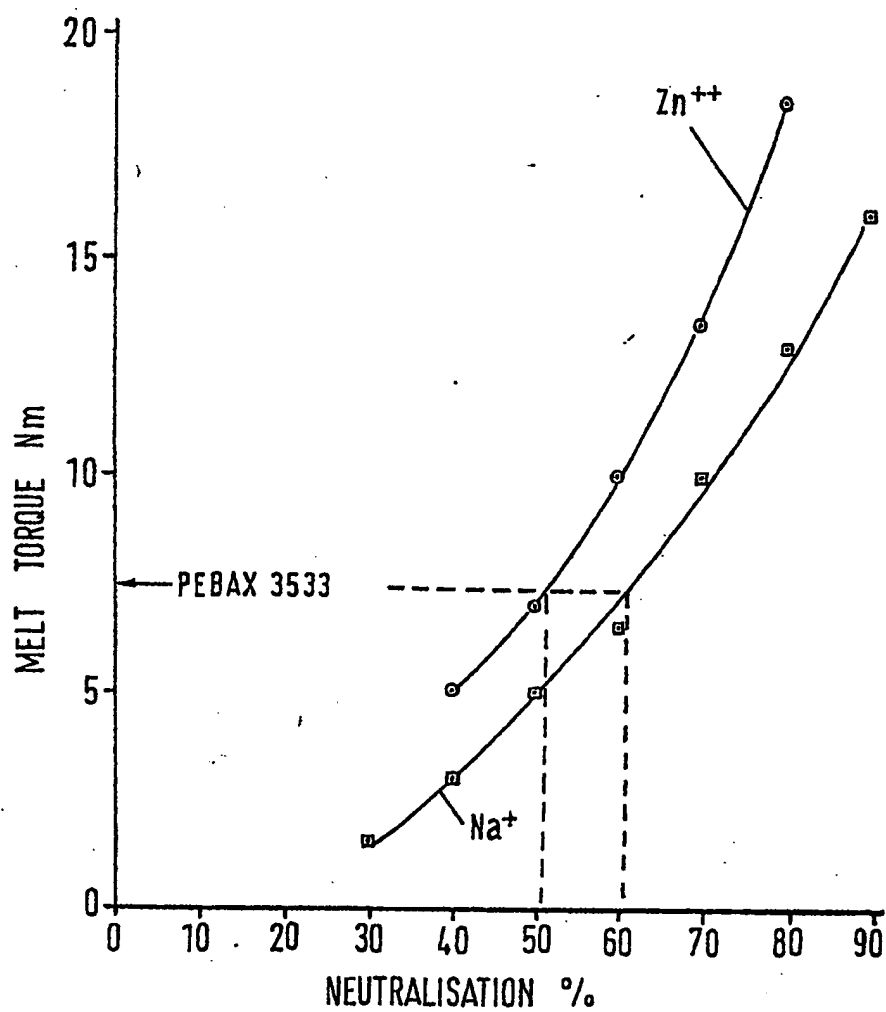
In preferred embodiments of the present invention, the total neutralisation level in said copolymer (i), (ii) or (iii) is at least 70%, preferably at least 80% and especially at least 90%. The preferred size of the powdered copolymer (iii) is a maximum of 100 microns for at least 85% of the copolymer. Suitably, the copolymer (iii) may have a modal particle size of 40 microns.

The mouldable composition can be used to make a homogeneous solid one-piece golf ball, a homogenous solid core for a two-piece golf ball or a core component for a multi-component golf ball.

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SPECIFICATION

Mouldable compositions

- 5 This invention relates to mouldable compositions, in particular to mouldable compositions which are suitable for use in the manufacture of homogeneous solid one-piece golf balls, homogeneous solid cores for two-piece golf balls or core components for multi-component golf balls, and to golf balls or cores obtained therefrom. 5

A solid one-piece golf ball comprises a moulded homogenous sphere of the required weight and dimensions, the moulding process including the provision of dimples on the outermost surface of the ball. 10
A two-piece golf ball comprises a moulded spherical core enclosed in an outer cover, the cover being provided with dimples on its outermost surface. 10

Apart from dimple design, the properties which most affect the dynamic performance of a golf ball are hardness and resilience. The hardness of the ball can affect the 'feel' of the ball on striking and the sound or 'click' produced. Resilience directly determines the ball speed off the club and, coupled with the dimple pattern, is the major factor determining flight distance. 15

In the present construction of two-piece golf balls, much of the ball performance, in terms of resilience, is derived from the core. Most top-quality two-piece balls utilise a peroxide-cured elastomeric composition based on a high *cis*-1,4- content polybutadiene and containing polymerisable metal salt monomers, typically the zinc salts of acrylic and methacrylic acid. 20

The 'fine tuning' of such core formulations over many years has resulted in two-piece balls which can now out-perform the traditional thread-wound construction and which are almost on the limit of performance, set by the governing bodies of golf in order to preserve the present character of the game. Thus a speed off the club of 255 ft.s⁻¹ (77.2 m.s⁻¹), under standard impact conditions, is the maximum currently permitted. 25

Various tests can be used to rate the performance of golf balls or cores for development and production control purposes etc. In the present description and claims, hardness and resilience are measured as follows:

Hardness is determined as deformation of the ball or core, in units of 0.001 inches (0.0254 mm) under a load of 87.5 lbs (39.69 Kg) for cores and 91.5 lbs (41.54 Kg) for balls, applied across a diameter. 30

Resilience is determined as Newton's coefficient of restitution (E) and is calculated from photo-electronic measurement of the ball or core and of a pneumatically-projected missile, before and after impact. The speed of impact is 180 ft.s⁻¹ (54.9 m.s⁻¹).

Accordingly, the present invention provides a mouldable composition comprising a blend of a resilient thermoplastics material and 35

either (i) a potentially-ionisable copolymer of ethylene and an α , β -unsaturated carboxylic acid which is ionised subsequent to the formation of the blend;

or (ii) an ionic copolymer of ethylene and an α , β -unsaturated carboxylic acid which is further ionised subsequent to the formation of the blend;

or (iii) an ionic copolymer of ethylene and an α , β -unsaturated carboxylic acid which is substantially ionised and which is powdered prior to the formation of the blend, in which the powdered copolymer (iii) has a maximum particle size of 200 microns and the total neutralisation level in said copolymer (i), (ii) or (iii) is at least 60%. 40

In preferred embodiments of the present invention, the total neutralisation level in said copolymer (i), (ii) or (iii) is at least 70%, preferably at least 80% and especially at least 90%. The preferred particle size of the powdered copolymer (iii) is a maximum of 100 microns for at least 85% of the copolymer. Suitably, the copolymer (iii) may have a modal particle size of 40 microns. 45

The present invention also provides a homogeneous solid one-piece golf ball, a homogeneous solid core for a two-piece golf ball and a core component for a multi-component golf ball, said ball and said cores being made of a mouldable composition as described in the immediately-preceding paragraph. 50

In a further preferred embodiment of the present invention, the Viscosity Index (as hereinafter defined) of the said copolymer (i) or (ii) should be equal to or greater than that of the said resilient thermoplastics material, immediately prior to the formation of the blend. If necessary, the Viscosity Index of the copolymer (i) or (ii) may be adjusted so that it attains the required level, e.g. by neutralisation of a proportion of the acid groups as described hereinbelow: 55

By 'Viscosity Index' is meant the value which relates to the melt viscosity of the individual blend components when subjected to the conditions of temperature and shear rate encountered, for example, in an internal mixer used to form the blend.

These conditions can be simulated using a Brabender Plastograph (PL3S) equipped with a cam mixing chamber (type N 50 H) and the Viscosity Index is quoted as the melt torque reading observed under the desired conditions of temperature and shear rate. 60

The resilient thermoplastics material can be, for example, a polyester block copolyamide, a copolyester, an ionic elastomer, a poly (1,2-polybutadiene) or a styrene/ethylene/butylene/styrene block copolymer.

The copolymer (i), (ii) or (iii) can be, for example, a copolymer of ethylene and methacrylic or acrylic 65

acid.

Ionisation of the copolymer (i), (ii) or (iii) can be achieved by means of suitable cation-supplying materials such as salts of metals from Groups I to IV of the Periodic Classification, e.g. sodium methoxide, zinc, xide, zinc acetate or magnesium acetate.

- 5 We have further found that the mouldability of the blend is greatly enhanced by having a blend micro-structure in which the copolymer (i), (ii) or (iii) is in the form of discrete particles which are dispersed in a matrix of the resilient thermoplastics material.

The present invention will be illustrated by way of the following Examples.

- 10 In the Examples, *Examples 1 to 6* show the use of copolymers of types (i) and (ii) according to the present invention and *Example 7* shows the use of a copolymer of type (iii).

Example 1

A core for a two-piece golf ball was made from a blend of the following materials :

- 15 (i) Material A - an ionic copolymer of ethylene and methacrylic acid in which about 30% of the acid groups had been neutralised by means of a sodium cation-supplying material, available from El Du Pont de Nemours & Co as SURLYN 1605 (SURLYN is a Registered Trade Mark).

(ii) Materials B - a polyester block copolyamide available from Atochem as PEBAX 3533 (PEBAX is a Registered Trade Mark).

- 20 35g of Material A and 65 g of Material B were melt-blended together in a Brabender internal mixer at 180°C until homogenous. Aliquots of the blend were moulded into spheres of 1.5" (38.1 mm) diameter and tested for compression and for resilience, i.e. coefficient of restitution (COR), as hereinbefore described. The results, together with comparative values for control cores moulded from Materials A and B, are given in Table 1 below.

TABLE 1

| | Compression | Resilience (COR) |
|-----------------------|-------------|---------------------|
| Material A (Control) | 18 | 0.657 |
| Material B (Control) | 112 | 0.571 |
| Blend (A + B) (35:65) | 46 | 0.618 |

35 The compression values of the control show that Material A produces a very hard core whilst Material B produces a very soft core. The blend, however, produces a sphere of intermediate compression which is acceptable as a golf ball core in a two-piece ball.

40 Examples 2-5

Cores for a two-piece golf ball were made from the following materials and using the following procedure:

Material A - A copolymer of ethylene and acrylic acid believed to contain

20% by weight of copolymerised acid - available from Dow Chemical Co as EAA 433 (PRIMACOR 5980)

- 45 (PRIMACOR is a Registered Trade Mark).

Material B - PEBAX 3533 (as described in Example 1). The formulations shown in Table 2 were prepared using the following procedure:

- 50 The indicated parts by weight of Materials A and B were charged into an internal mixer, heated to 180°C, and blended for 2 minutes. To the melt was then added sufficient quantity of a cation-supplying material to neutralise all of the acid groups in the blend. Mixing was continued until all visible signs of a reaction (i.e. evolution of gas) had ceased.

Golf ball cores moulded from the compositions had the properties shown in Table 2.

TABLE 2

| | | (parts by weight) | | | | |
|----|--|--------------------|------------------|-------|-------|----|
| 5 | Example | 2 | 3 | 4 | 5 | 5 |
| | Formulation | | | | | |
| | Ethylene-acrylic acid copolymer | 50 | 50 | 70 | 70 | |
| | Polyether copolyamide | 50 | 50 | 30 | 30 | |
| 10 | Neutralising agent | | | | | |
| | (Cation-supplying-) | | | | | |
| | (material) | (Zinc oxide | | | | 10 |
| | | 6.0 | | | | |
| | | (Sodium methoxide | 7.5 | | | |
| | | (Zinc acetate | | 21.3 | | |
| | | (Magnesium acetate | | | 17.4 | |
| 15 | Core properties | | | | | 15 |
| | Compression | 38 | 40 | 30 | 24 | |
| | Resilience (COR) | 0.691 | 0.635 | 0.688 | 0.679 | |
| 20 | Example 6 | | | | | 20 |
| | The relationship between melt viscosity and degree of neutralisation of the ethylene/acrylic acid copolymer of Example 2 was determined by measurement of melt torque using a Brabender Plastograph (PL3S). The mixing chamber employs twin rotors with speed differential 1 : 1.5 and is said to simulate | | | | | |
| 25 | the mixing action of a Banbury-type internal mixer. | | | | | 25 |
| | Neutralisation was achieved by the addition of zinc acetate or sodium methoxide to the melt. | | | | | |
| | Values of melt torque were observed after completion of the reaction at a rotor speed of 60 rpm and a final melt temperature of 170°C. | | | | | |
| | The melt viscosity of the copolyamide PEBAX 3533 was similarly determined. | | | | | |
| 30 | The results of these determinations are expressed in the graph attached hereto and labelled Figure 1. | | | | | 30 |
| | This shows that for the equivalent melt torque in forming a blend of the copolyamide PEBAX 3533 and the copolymer EAA 433 (PRIMACOR 5980) it is necessary that approximately 52% of the copolymer acid groups are neutralised by zinc cations. | | | | | |
| 35 | 2200 g of the ethylene-acrylic acid copolymer of Example 2 was charged into an internal mixer, pre-heated to about 120°C, and mixed until fluxed. 404 g of zinc acetate dihydrate (sufficient to neutralise about 60% of the available acid groups) was added to the molten copolymer and mixing continued until evidence of a reaction had ceased. During this time the melt temperature increased to about 180°C. The material was then dumped and sheeted off on a two-roll mill. | | | | | 35 |
| 40 | 1050 g of the partially neutralised acid copolymer and 1440 g of the polyether co-polyamide PEBAX 3533 were charged into a pre-heated Banbury internal mixer operating at rotor speeds of 60 - 75 rpm and 120°C and mixed till fluxed and thoroughly blended, the final temperature reaching 170°C. A further 118 g of zinc acetate dihydrate was then added to the blend to neutralise substantially all of the remaining acid groups. When mixing was complete, the material was dumped, sheeted and granulated. The granulated material was formed into smooth spheres of 1.55" (39.37 mm) and 1.68" (42.67 mm) diameters by a process of injection moulding. The spheres were of good quality and yielded the following test results: | | | | | 40 |
| 45 | | | | | | 45 |
| | Diameter | 1.55" (39.37 mm) | 1.68" (42.67 mm) | | | |
| | Compression | 43 | 46 | | | |
| | Resilience (COR) | 0.666 | 0.660 | | | |
| 50 | | | | | | 50 |
| | Example 7 | | | | | |
| | A composition according to the invention was prepared by the following procedure: | | | | | |
| 55 | A latex dispersion of the ethylene-acrylic acid copolymer of Example 2 was prepared by agitating a mixture of 100 g of the copolymer, 1000 ml of de-ionised water and 30 ml of ammonia solution (27% NH ₃) at 95°C for 20-30 minutes. After all of the solid copolymer had dispersed, the dispersion was cooled to ambient temperature. 32 g of zinc acetate was dissolved in 1000 ml of water and this solution slowly added to the latex dispersion whilst agitating the mixture. The resultant mixture was filtered and there was recovered a particulate material in 'wet-cake' form. This was dried in an oven at 50°C, broken into small lumps and passed through an ultra-centrifugal mill fitted with a 1200 micron screen to further break down the agglomerated material. Photomicrographic study showed the particle size of the resultant material to be in the range 0-200 microns, with 85% below 100 microns and a modal value of 40 microns. | | | | | 55 |
| 60 | Analysis of the particulate material by Infra Red Spectrophotometry indicated that 60% of the acid groups had been neutralised by the zinc salt. | | | | | 60 |
| 65 | The particulate material showed no sign of melting or fusing together when sprinkled on a metallic | | | | | 65 |

plate heated to 160°C. 50 g of a polyether-copolyamide, PEBAX 3533, was charged into an internal mixer at 160°C and mixed until fluxed. 50 g of the aforementioned particulate material was added and mixing continued until the particulate material was thoroughly dispersed in the copolyamide. The composition was then removed from the mixer and formed into golf ball cores by compression moulding in a 1.625" (41.275 mm) diameter spherical mould. These cores were tested and the following properties recorded:

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|------------------|-------|
| Compression | 48 |
| Resilience (COR) | 0.687 |

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CLAIMS

1. A mouldable composition comprising a blend of a resilient thermoplastics material and *either* (i) a potentially-ionisable copolymer of ethylene and an α , β -unsaturated carboxylic acid which is ionised subsequent to the formation of the blend; 15
- or (ii) an ionic copolymer of ethylene and an α , β -unsaturated carboxylic acid which is further ionised subsequent to the formation of the blend;
- or (iii) an ionic copolymer of ethylene and an α , β -unsaturated carboxylic acid which is substantially ionised and which is powdered prior to the formation of the blend, in which the powdered copolymer (iii) has a maximum particle size of 200 microns and the total neutralisation level in said copolymer (i), (ii) or (iii) is at least 60%. 20
2. A composition according to Claim 1, in which at least 85% of the powdered copolymer (iii) has a maximum particle size of 100 microns.
3. A composition according to Claim 2, in which the powdered copolymer (iii) has a modal particle size of 40 microns. 25
4. A composition according to Claim 1, 2, or 3 in which the total neutralisation level in said copolymer (i), (ii) or (iii) is at least 70%.
5. A composition according to any one of claims 1 to 4, in which the total neutralisation level is at least 80%. 30
6. A composition according to any one of Claims 1 to 5, in which the total neutralisation level is at least 90%.
7. A composition according to any one of Claims 1 to 6, in which the copolymer is (i) or (ii) and in which the Viscosity Index (as hereinbefore defined) of the said copolymer (i) or (ii) is equal to or greater than that of the said resilient thermoplastics material, immediately prior to the formation of the blend. 35
8. A composition according to any one of the preceding claims, in which the resilient thermoplastics material is a polyester block copolyamide, a copolyester, an ionic elastomer, a poly(1,2-poly-butadiene) or a styrene/ethylene/butylene/styrene block copolymer.
9. A composition according to any one of the preceding claims, in which the copolymer (i), (ii) or (iii) is a copolymer of ethylene and methacrylic or acrylic acid. 40
10. A composition according to any one of the preceding claims, in which the ionisation or further ionisation of the copolymer (i), (ii) or (iii) is achieved by means of a cation-supplying material.
11. A composition according to Claim 10, in which the cation-supplying material is a salt of a metal from Groups I to IV of the Periodic Classification.
12. A composition according to Claim 11, in which the cation-supplying material is sodium methoxide, zinc oxide, zinc acetate or magnesium acetate. 45
13. A composition, substantially as hereinbefore described with reference to any one of the Examples.
14. A moulded product formed from a composition according to any one of the preceding claims.
15. A moulded product according to Claim 14, which is a homogeneous solid one-piece golf ball.
16. A moulded product according to Claim 14, which is a homogenous solid core for a two-piece golf ball. 50
17. A moulded product according to Claim 14, which is a core component for a multi-component golf ball.

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